Appl Nanosci (2013) 3:211–215
DOI 10.1007/s13204-012-0108-6

ORIGINAL ARTICLE

Effect of calcium oxalate on the photocatalytic degradation of Orange II on ZnO surface

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Received: 31 January 2012 / Accepted: 24 March 2012 / Published online: 25 April 2012

Abstract The photocatalytic degradation of aqueous solution of Orange II, has been investigated in the presence of ZnO catalyst with calcium oxalate as sacrificial agent. This study demonstrated that the performance of ZnO photocatalyst can be improved by addition of calcium oxalate. Results show that adsorption is an important parameter controlling the degradation phenomena. Indeed, the added oxalate causes a drop in the pH medium, what causes a better adsorption of Orange II on the ZnO surface. The effect of calcium oxalate is to increase the concentration of superoxides ($O_2^{\cdot-}$) and hydroperoxides ($HO_2\cdot$) radicals, which are key intermediaries in the mechanism of photodegradation because of their powerful force of oxidation.

Keywords ZnO · Photocatalysis · Organic pollutants · Orange II · Photocatalytic degradation · Sacrificial agent

Introduction

Heterogeneous photocatalysis is an efficient technique to destroy organic pollutants in water (Rajeshwara et al. 2008; Garcia et al. 2009). The basic process of photocatalysis consists in ejecting an electron from the valence band (VB) to the conduction band (CB) of the semi-conductor thus creating h^+ hole in the valence band. This is followed by the formation of extremely reactive radicals such as OH· at the semiconductor surface or by direct oxidation of the polluting species by h^+. On the other hand, electrons are trapped at surface sites which reacted with electron acceptors such as oxygen adsorbed or dissolved in water to form superoxide radical $O_2^{\cdot-}$. TiO_2 and especially anatase form, is considered as an excellent photocatalyst that can mineralize a large range of organic pollutants (Mills and Le Hunte 1997, Agrios and Pichat 2005, Lewandowski and Ollis 2004). This semi-conductor is the most studied material for such applications (Neppolian et al. 2002). Alternatively, ZnO can be considered as the second photocatalyst after TiO_2, whose physical–chemical properties are comparable to those of TiO_2 (Liqiang et al. 2004, Behnajady et al. 2006, Akyol and Bayramoylu 2005, Anandan et al. 2010). However, as mentioned by Liqiang et al. 2004, semiconductor photocatalysts, other than TiO_2, are much less studied. Furthermore, ZnO nanoparticle is stable and easy to be prepared.

One of the limiting factors that control the photocatalysts' efficiency is the rapid recombination of photogenerated electron–hole pairs in semi-conductor particles. Currently, many studies are realized to limit this phenomenon. Among the proposed solutions are to be found:

- Coupling with another appropriate semi-conductor (Robert 2007, Helaili et al. 2010),
- Chemical doping with atoms such as nitrogen (Gole et al. 2004), carbon (Sakhtivel and Kisch 2003) or thallium (Kong et al. 2010),
- Addition of electron acceptors such as dissolved oxygen (Laisheng et al. 2003)

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- Or addition of soluble organic sacrificial agents such as methanol (Patsouras et al. 2007).

In a recent paper, we have proposed to incorporate a sacrificial agent insoluble in water with photocatalyst such as calcium oxalate (Bassaid et al. 2009). The role of oxalate ions is to react with photogenerated holes to limit their recombination with photogenerated electrons. In the current study, we show the effect of calcium oxalate on the photocalytique properties of ZnO for the removal of organic pollutants in water. Orange II is used as an organic pollutant model that will evaluate the effect of the addition of $Ca(COO)_2$ on the photocatalytic performance of ZnO.

Experimental

Reagents

All the reagents used in this work were of analytical grade and were used in their as-received state: calcium chloride (Fluka 99 %), ammonium oxalate (Merck 99 %) and Orange II (Sigma Chemical Co.). Zinc oxide (Riedel–de haen, 99.95 % purity, particles size was 50 nm and ZnO phase is hexagonal structure: Wurtzite). The specific surface area of ZnO was determined by Brunauer, Emmett and Teller (BET) method using nitrogen gas as the adsorbent at 77 K on ASAP 2010 Micrometrics Apparatus. The specific area is 74.3 $m^2\ g^{-1}$.

Calcium oxalate $Ca(COO)_2$ was prepared by mixing aqueous solution of ammonium oxalate (0.5 M) and calcium chloride (0.5 M). The precipitate of calcium oxalate obtained is filtered, washed with water and dried in air at 110 °C overnight.

Adsorption experiments

All adsorption equilibrium experiments of Orange II on the ZnO and ZnO/20 % $Ca(COO)_2$ sample surface were carried out in batch mode under dark conditions. Studies were made using suspensions prepared by mixing a 50-ml solution of various initial concentrations of Orange II at their natural pH and ZnO concentration of 0.5 $g\ l^{-1}$ (in distilled water). The equilibrium concentrations of Orange II in the solutions were studied after centrifugation by measuring the change in absorption intensity at this λ_{max} (484 nm) using a PHILIPS Vis-spectrophotometer.

Irradiation experiments

Photocatalytic experiments were performed in a double-walled reactor placed on the 125 W mercury lamp (TUNGSRAM) as a light source. The operating temperature was fixed during the experiment at 25 °C by a circulation of water. Pure ZnO and ZnO with an appropriate weight of calcium oxalate (total weight = 50 mg) were dispersed through stirring in a volume of 100 ml of Orange II aqueous solution (10 mg/l) and 5 ml of aliquot was taken out at regular time intervals. The samples were noted TiO_2/X%$Ca(COO)_2$ with "X" represents the percentage of $Ca(COO)_2$ in the composite. The value of the percentage corresponds to the percentage in weight of $Ca(COO)_2$ in the composite. Before each irradiation, the solutions were maintained in the dark for 1 h to reach the adsorption equilibrium. For analysis, each sample containing catalyst was centrifuged prior and analyzed by Vis-spectrophotometer (PHILIPS) (λ_{max} = 484 nm).

Results and discussion

Effect of calcium oxalate loading on the photocatalytic activity of ZnO

The effect of the partial replacement of ZnO by calcium oxalate on the disappearance kinetics of Orange II was investigated. The percentage of calcium oxalate increases from 0 to 50 % in weight for a total concentration of ZnO + calcium oxalate constant and equal to 500 mg/l. All experiments were first carried out in dark during 60 min, and then immediately irradiated by UV–Vis irradiation until complete decolorization of the compound. Figure 1 shows the effect of oxalate calcium on the photocatalytic decolorization of Orange II with ZnO under irradiation.

The photodecomposition of Orange II was subjected to photochemical degradation depending on the model of Langmuir–Hinshelwood kinetics appears to be followed satisfactorily. The photocatalytic degradation of Orange II follows a kinetic of pseudo-first order. For a low initial dye concentration, the simplest representation for the rate of photodegradation of Orange II is given by $\ln C_t = -kt + \ln C_0$.

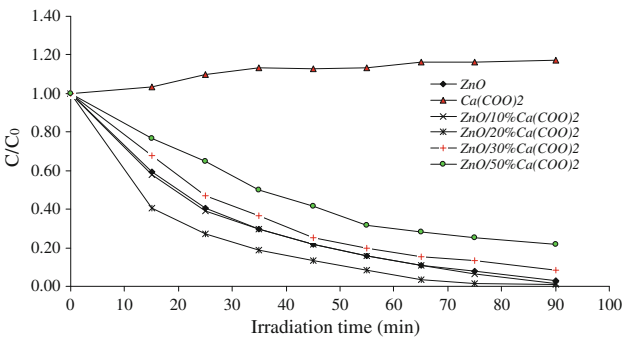

Fig. 1 Effect of calcium oxalate on the photocatalytic degradation of Orange II ([OII] = 10 mg/l) in the presence of ZnO at natural pH

This equation can be used to demonstrate the linearity of data. His integration is given by $\mathrm{Ln}(C_0/C_t) = kt$ where k is the constant of the pseudo-first-order rate.

The obtained constant (k) and half-life ($t_{1/2}$) have been listed in Table 1, which reveal a significant and favorable effect of added oxalate calcium on the photocatalytic decolorization of Orange II dye with ZnO. The k and $t_{1/2}$ for ZnO/20 % $Ca(COO)_2$ showing the good photocatalytic activity, are equal to 5.10×10^{-2} min^{-1} and 13.6 min, respectively.

Adsorption results

To obtain an explanation for the effect of the oxalate on the photodegradation of Orange II by ZnO, isotherm adsorption of pure ZnO and 80 % ZnO/20 % oxalate mixtures was studied. As mentioned earlier, adsorption phenomena on catalysts are of prime importance for the degradation of organic molecules.

Adsorption isotherm results of Orange II show very good adsorption onto ZnO and 80 % ZnO/20 % oxalate mixtures in aqueous solution compared to that of calcium oxalate alone. Langmuir adsorption model has been applied to describe the adsorption of Orange II on materials. It is given as the classical following equation:

$$Q = Q_{ads}/Q_{max} = \frac{K_{ads}C_{eq}}{1 + K_{ads}C_{eq}}$$

where Q is the ZnO surface coverage, Q_{ads} the adsorbed quantity, Q_{max} the adsorption maximum capacity of Orange II on the ZnO surface (mg/g), C_{eq} the concentration of Orange II at the adsorption equilibrium and K_{ads} the Langmuir adsorption constant. The linear transform is given in Fig. 2. The Langmuir parameters for Orange II adsorbed on various material samples are reported in Table 2.

The results show that the maximum capacity adsorption (Q_m) of Orange II on the mixed ZnO/$Ca(COO)_2$ catalysts increases with oxalate weight. The value of Q_m is still higher than that of pure ZnO and pure oxalate in the case of the mixture 80 % ZnO/20 % $Ca(COO)_2$. This can be explained by the effect of the pH of medium. It is well known now that the adsorption of the dyes on the material semiconductors strongly depends on the pH of mediums (Bassaid et al. 2009; Kiriakidou et al. 1999). The natural pH of ZnO/Orange II solution is 6.8. The pH of zero point of charge for ZnO is about 9 (Sakthivel et al. 2003).

In the presence of water molecules, ZnO particles are covered by hydroxide groups. However, if the pH of the medium varies, these OH groups are able to give or tear off protons H^+. Figure 3 shows the modification of the ZnO charge surface according to the pH. In different pH ranges, there exist electrostatic interaction (attraction or repulsion) between the catalyst surface and the dye molecules. This phenomenon can have an effect on adsorption and consequently on photocatalytic degradation. Indeed, after added oxalate, we obtained a pH 6.1. This pH is lower than the pHzpc, which gives to the surface of catalyst a positive load. Consequently, a strong attraction between catalyst and Orange II, since this last is dye anionic, which leads to a strong adsorption of the Orange II on the surface of catalyst.

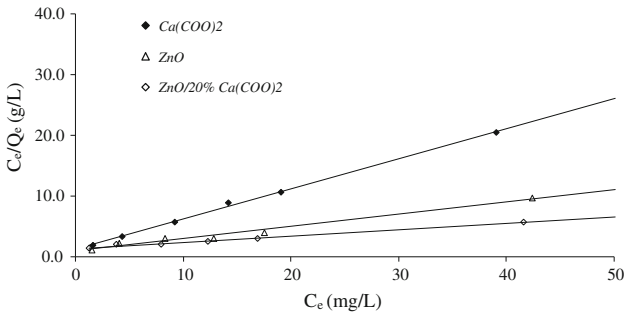

Fig. 2 Linearization of Langmuir isotherm of Orange II on ZnO and calcium oxalate

Table 1 First-order-rate constant (k) and half life ($t_{1/2}$) for the photocatalytic degradation of Orange II using ZnO with oxalate calcium

Catalysts	k_{app} (min^{-1})	$t_{1/2}$ (min)	R^2
ZnO	3.50×10^{-2}	19.8	0.99
ZnO/10 % $Ca(COO)_2$	3.80×10^{-2}	18.2	0.95
ZnO/20 % $Ca(COO)_2$	5.10×10^{-2}	13.6	0.98
ZnO/30 % $Ca(COO)_2$	2.80×10^{-2}	24.8	0.99
ZnO/50 % $Ca(COO)_2$	1.80×10^{-2}	38.5	0.98

Table 2 Adsorption isotherm parameters of Orange II on ZnO and mixed ZnO/calcium oxalate materials

Catalysts	$Ca(COO)_2$	ZnO	ZnO/20 % $Ca(COO)_2$
Q_m (mg/g)	1.967	5.051	9.615
K_L (L/mg)	0.450	0.200	0.078
R^2	0.99	0.98	0.99

Effect of calcium oxalate on the mechanism of Orange II photodegradation on ZnO

In the previous work (Bassaid et al. 2009), we described the photocatalytic degradation mechanism of Orange II in the presence of the TiO_2 semiconductor. In the case of ZnO, the mechanism is similar. The first step is the photogeneration of the h^+/e^- pair by an appropriate irradiation of ZnO.

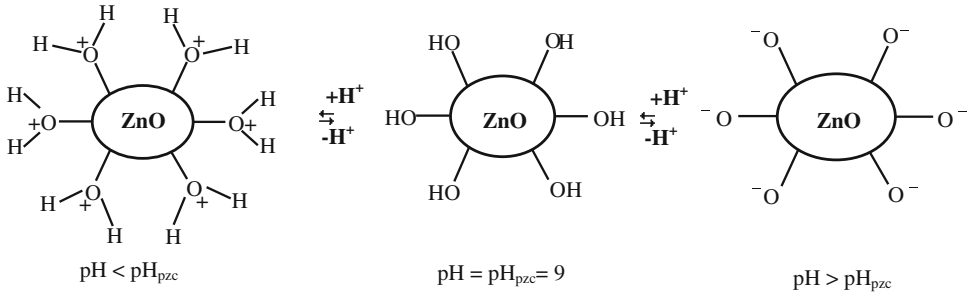

Fig. 3 Modification charge of surface of ZnO according to the pH in different pH ranges

$$ZnO + h\upsilon \rightarrow e^{-}_{CB} + h^{+}_{VB}$$

The holes h^+ react then with electron donors, such as water and $OH^{\cdot -}$ ions adsorbed on the surface of catalyst, to form hydroxyl radicals (like $OH^{\cdot}$) and/or a direct oxidation of the polluting species. The electrons, as for them, react with electron acceptors such as oxygen adsorbed, to form $O_2^{\cdot -}$ radicals. The main effect of $Ca(COO)_2$ is to promote the adsorption of Orange II on the catalyst surface by lowering the pH of the solution.

On the other hand, calcium oxalate is oxidized by reaction with a valence band hole giving rise to a radical oxalate and to yield carbon dioxide and $CO_2^{\cdot -}$ radical (Farouzan et al. 1996).

$$^{-}OOC\text{-}COO^{-} + h^{+}_{VB} \rightarrow {}^{-}OOC\text{-}COO^{\cdot}$$

$$^{-}OOC\text{-}COO^{\cdot} \rightarrow CO_2 + CO_2^{\cdot -}$$

$CO_2^{\cdot -}$ and oxalate radicals react with molecular oxygen yielding $O_2^{\cdot -}$, where $O_2^{\cdot -}$ is in equilibrium with HO_2 ($pKa = 4.8$ (Patsouras et al. 2007). Superoxide and hydroperoxyl radicals ($O_2^{\cdot -}/HO_2$) are key intermediates because of their strong oxidizing power, which degrades Orange II compound.

These results confirm those concerning the effect of calcium oxalate with the P25-TiO_2 in our previous study (Bassaid et al. 2009). The best efficiencies are obtained with 20 and 30 % calcium oxalate, respectively for ZnO and TiO_2. If we consider the ratio k_2/k_1 (with k_1 and k_2: apparent rate constants for pure TiO_2 (or ZnO) and 70 % TiO_2/30 % $Ca(COO)_2$ (or 80 % TiO_2/20 % ZnO), respectively), we find 1.45 for ZnO and 1.32 for TiO_2-P25.

The specific area of the two photocatalysts (50 m^2/g for TiO_2 and 67 m^2/g for ZnO) and the band gap values are very close (3.2 and 3.3 eV), which could explain these results.

Conclusion

We showed that it was possible to improve the activity of the ZnO photocatalyst by combining it with oxalate of calcium $Ca(COO)_2$ for the photocatalytic degradation of Orange II. The results of this study show that the sacrificial agent $Ca(COO)_2$ plays a significant role in the adsorption of Orange II on the surface of the ZnO catalyst. In our conditions, the optimum ratio is 20 % $Ca(COO)_2$/80 % ZnO. An increase in the amount of oxalate above 20 % causes a decrease in the photocatalytic activity of the mixture. The calcium oxalate presence allows increasing the concentration of reactive species in the solution such as superoxides and hydroperoxides radicals.

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